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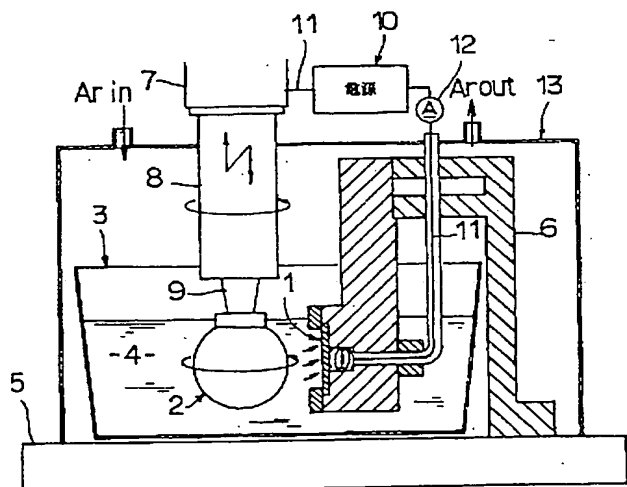
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(54) 【発明の名称】 超純水中の水酸基による加工方法

(57) 【要約】

【課題】 超純水中の OH^- 濃度を増大させれば、この OH^- を利用して十分に加工することができるとの認識に基づき、超純水中の OH^- を用いて被加工物の加工面に不純物を残さずに清浄な加工が行える全く新しい超純水中の水酸基による加工方法を提供する。

【解決手段】 微量の不可避不純物を除き超純水のみを用い、これにイオン積を増大させる水酸基増加処理を施し、この水酸基又は水酸基イオンの濃度が増大した超純水中に浸漬した被加工物を、水酸基又は水酸基イオンによる化学的溶出反応若しくは酸化反応によって除去加工若しくは酸化被膜形成加工する。



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【特許請求の範囲】

【請求項1】 微量の不可避不純物を除き超純水のみを用い、これにイオン積を増大させる水酸基増加処理を施し、この水酸基又は水酸基イオンの濃度が増大した超純水中に浸漬した被加工物を、水酸基又は水酸基イオンによる化学的溶出反応若しくは酸化反応によって除去加工若しくは酸化被膜形成加工することを特徴とする超純水中の水酸基による加工方法。

【請求項2】 前記水酸基増加処理として、超純水中に間隔を置いて配設した一対又はそれ以上の電極間に電流を流し、超純水を電気分解してなる請求項1記載の超純水中の水酸基による加工方法。

【請求項3】 前記水酸基増加処理として、超純水を高温、高圧に維持してなる請求項1記載の超純水中の水酸基による加工方法。

【請求項4】 前記水酸基増加処理として、超純水を高温、高圧に維持しながら、超純水中に間隔を置いて配設した一対又はそれ以上の電極間に電流を流し、超純水を電気分解してなる請求項1記載の超純水中の水酸基による加工方法。

【請求項5】 前記水酸基増加処理として、超純水中に配設したイオン交換機能又は触媒機能を有する固体表面での電気化学反応を利用してなる請求項1記載の超純水中の水酸基による加工方法。

【請求項6】 前記水酸基増加処理として、超純水に誘電損失の可及的小さな周波数の高周波電圧を印加して水プラズマを生成し、水を電離又は解離させてなる請求項1記載の超純水中の水酸基による加工方法。

【請求項7】 前記被加工物を陽極とし、又は被加工物の電位を高く維持して、該被加工物の表面に水酸基イオンを引き寄せてなる請求項1～6何れかに記載の超純水中の水酸基による加工方法。

【発明の詳細な説明】

【0001】

【発明の属する技術分野】本発明は、超純水中の水酸基による加工方法に係わり、更に詳しくは超純水のみを用いて、そのイオン積を増大させて水酸基又は水酸基イオンによって被加工物を除去加工若しくは酸化被膜形成加工することができる加工方法に関する。

【0002】

【従来の技術】近年、科学技術の発展のもとに新材料の開発が次々と進んでいるが、それらの新材料に対する有効な加工技術は未だ確立されておらず、常に新材料開発の後を追う立場となっている。

【0003】また、最近ではあらゆる機器の構成要素において微細化且つ高精度化が進み、サブミクロン領域での物作りが一般的となるにつれて、加工法自体が材料の特性に与える影響はますます大きくなっている。このような状況下では、従来の機械加工のように工具が被加工物を物理的に破壊しながら除去していく加工法では、加

工によって被加工物に欠陥を多く生み出してしまうため、被加工物の特性は劣化する。従って、いかに材料の特性を損なうことなく加工を行うことができるかが問題となってくる。

【0004】この問題を解決する手段として先ず開発された特殊加工法に、化学研磨や電解加工、電解研磨がある。これらの加工法は従来の物理的な加工とは対照的に、化学的溶出反応を起こすことによって除去加工を行うものである。従って、塑性変形による加工変質層や転位等の欠陥は発生せず、前述の材料の特性を損なわずに加工を行うといった問題は解消される。

【0005】そして、更に注目されているのが、原子間の化学的な相互作用を利用した加工法である。これは、微粒子や化学反応性の高いラジカル等を利用したものである。これらの加工法は、被加工物と原子オーダでの化学反応により除去加工を行うため原子オーダの加工制御が可能である。この加工法の例としては、本発明者が開発したEEM(Elastic Emission Machining)(特開平1-236939号公報)やプラズマCVM(Cheical Vaporization Machining)(特開平1-125829号公報等)がある。EEMは、微粒子と被加工物間の化学反応を利用したもので、材料の特性を損なうことなく原子オーダの加工を実現している。また、プラズマCVMは、大気圧プラズマ中で生成したラジカルと被加工物とのラジカル反応を利用したもので、原子オーダの加工を実現している。

【0006】

【発明が解決しようとする課題】ところで、前述の電解加工や電解研磨では、従来は被加工物と電解液(NaCl、NaNO₃、HF、HCl、HNO₃、NaOH等の水溶液)との電気化学的相互作用によって加工が進行するとされている。また、電解液を使用する限り、その電解液で被加工物が汚染されることは避けられない。

【0007】そこで、本発明者は、中性及びアルカリ性の電解液では水酸基(OH⁻)が加工に作用していると考え、それならば微量ながらOH⁻が存在している水によっても加工はできるとの仮定に至った。超純水中のOH⁻を利用して加工ができれば、加工面に不純物を残さない清浄な加工が行え、その用途は半導体製造分野をはじめ、非常に広いと予測される。しかし、超純水中に含まれるOH⁻濃度は、非常に希薄で、25℃、1気圧において10⁻⁷mol/l程度であることは周知の事実であり、例えば超純水中にSiを浸漬することで、エッチングが行われているといった内容の報告はこれまでのところない。

【0008】本発明が前述の状況に鑑み、解決しようとするところは、超純水中のOH⁻濃度を増大させれば、このOH⁻を利用して十分に加工することができるとの認識に基づき、超純水中のOH⁻を用いて被加工物の加工面に不純物を残さずに清浄な加工が行える全く新しい

加工方法を提供する点にある。

【0009】

【課題を解決するための手段】本発明は、前述の課題解決のために、微量の不可避不純物を除き超純水のみを用い、これにイオン積を増大させる水酸基増加処理を施し、この水酸基又は水酸基イオンの濃度が増大した超純水中に浸漬した被加工物を、水酸基又は水酸基イオンによる化学的溶出反応若しくは酸化反応によって除去加工若しくは酸化被膜形成加工することを特徴とする超純水中の水酸基による加工方法を提供する。

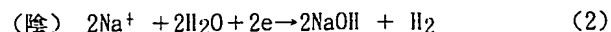
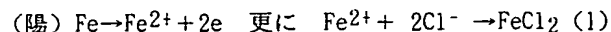
【0010】ここで、前記水酸基増加処理として、超純水中に間隔を置いて配設した一対又はそれ以上の電極間に電流を流し、超純水を電気分解してなること、あるいは超純水を高温、高圧に維持してなること、あるいは超純水を高温、高圧に維持しながら、超純水中に間隔を置いて配設した一対又はそれ以上の電極間に電流を流し、超純水を電気分解してなること、あるいは超純水中に配設したイオン交換機能又は触媒機能を有する固体表面での電気化学反応を利用してなること、あるいは超純水に誘電損失の可及的小さな周波数の高周波電圧を印加して水プラズマを生成し、水を電離又は解離させてなることを採用する。

【0011】そして、前述の水酸基増加処理と併用して、前記被加工物を陽極とし、又は被加工物の電位を高く維持して、該被加工物の表面に水酸基イオンを引き寄せて、被加工物近傍の水酸基イオンの濃度を高めて加工することが最も好ましい。

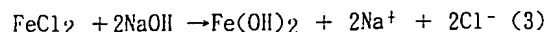
【0012】

【発明の実施の形態】本発明の超純水を利用した各種材料の加工方法の原点は、従来の電解加工での反応機構に対する疑問にある。電解加工 (Electrolytic Machining) は、電気化学的溶解作用 (陽極溶出又は電解溶出) を材料の所要部に集中・制限することにより、所要の形状、寸法、表面状態を得る加工方法である。具体的には、電解液中において所要の形状に作られた陰極を被加工物である陽極とギャップ 0.02 ~ 0.7 mm で対向させ、5 ~ 20 V の直流電圧 (電流密度は 30 ~ 200 A/cm²) を印加させて加工を行うものである。これらの条件によって、電解溶出を陽極の極近傍に集中・制限させて起こすことにより、被加工物を工具である陰極の形状を反転した形状に加工するのである。

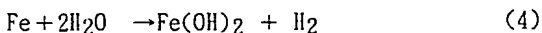
【0013】次に、従来の電解加工における反応機構の定説を簡単に説明する。例えば、電解液に NaCl 水溶液を用いて Fe の電解加工を行った場合、その両極での反応過程は一般には以下になるとされている。



こうして陰極で発生した NaOH と陽極で発生した FeCl₂ とが液中で反応して



となる。こうして式(1)から式(3)を辺々加えると、前反応式は、

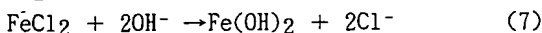
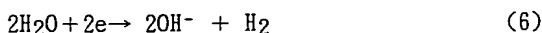


となる。

【0014】そこで、疑問とするのは、式(3)であり、この式においては、NaOHがこのままの形で FeCl₂ と反応しているように見える。しかし、NaOHについて Na はイオン化傾向が大きいので、電解液中においては NaOH は次の式(5)のように Na⁺ と OH⁻ とに電離していると考えられる。即ち、



となる。この過程を考慮すると、式(2)、式(3)は、それぞれ



となり、式(1)、式(6)、式(7)を辺々加えると、式(4)が同様に導かれる。

【0015】この式(1)から式(3)の反応過程と、式(1)→式(6)→式(7)の反応過程の両者を比較すると、前者において NaOH 自身がその反応に寄与しており、一方後者においては NaOH が電離することによって生じた OH⁻ が反応に寄与していることが分かる。即ち、後者は OH⁻ が存在すれば反応は進行すると考えられるのである。ここで、OH⁻ は溶液中だけでなく、単に純水な水の中にも微量 (25℃において 10⁻⁷ mol/l) ではあるが存在する。従って、上述の考えを基にすれば、超純水中の OH⁻ を利用することでアルカリ溶液中と同様の材料の加工が可能だということになる。

【0016】しかし、前述の如く、超純水中の OH⁻ は微量であるので、実用的な加工を可能にするには、何らかの方法で OH⁻ 濃度を増大させなければならない。本発明は、他の溶液を加えることなく、超純水中の OH⁻ 濃度を増大させて、極度に清浄化された環境での材料の加工を行うことにある。従って、本発明の加工では被加工物表面の汚染は生じない。

【0017】本発明の加工原理は、超純水中の水分子を電離し、生成された水酸基又は水酸基イオンを被加工物表面に供給し、被加工物原子と水酸基又は水酸基イオンとの反応によって、材料表面に清浄な酸化膜を形成したり、あるいは材料表面原子を除去し、その集積によって目的とする形状を得るものである。

【0018】つまり、加工工具となる水酸基又は水酸基イオンを、被加工物表面近くに設置された電極表面やイオン交換機能又は触媒機能を有する固体表面での化学反応によって生成すれば、このような水酸基又は水酸基イオンを発生する固体材料表面近傍の被加工物表面が優先的に加工される。従って、水酸基あるいは水酸基イオンを発生させる材料の形状を被加工物表面に転写する、いわゆる転写加工が可能である。また、水酸基あるいは水酸基イオンを発生させる材料の形状が線状である場合に

は、板状材料の切断加工が可能である。そして、水酸基又は水酸基イオンの供給量等の加工パラメータを調節することによって、材料表面で誘起される反応が酸化反応であるか、除去加工反応であるかを選択することが可能である。

【0019】本発明の加工方法において、加工速度（加工能率）を高めるために、水酸基増加処理が重要である。水酸基増加処理には、熱的に平衡な状態で OH^- を増加させる方法と、熱的に非平衡な（熱的平衡を利用しない）状態で OH^- を増加させる方法とがある。加工という観点から水酸基増加処理を見れば、 OH^- を局在させて加工領域を制限するには熱的平衡を利用しない方法で OH^- を増加させることが好ましいが、熱的に平衡な状態で OH^- を増加させても、 OH^- のみを分離あるいは集積して被加工物の加工面に供給できれば同様に加工領域を制限することが可能である。

【0020】その水酸基増加処理としては、超純水中に間隔を置いて配設した一対又はそれ以上の電極間に電流を流し、超純水を電気分解してなる処理（電解処理）、あるいは超純水を高温、高圧に維持してなる処理（高温高圧処理）、あるいは超純水を高温、高圧に維持しながら、超純水中に間隔を置いて配設した一対又はそれ以上の電極間に電流を流し、超純水を電気分解してなる処理（高温高圧・電解処理）、あるいは超純水中に配設したイオン交換機能を有する固体表面での電気化学反応を利用してなる処理（イオン交換処理）、超純水中に配設した触媒機能を有する固体表面での反応を利用してなる処理（触媒処理）、あるいは超純水に誘電損失の可及的小さな周波数の高周波電圧を印加して水プラズマを生成し、水を電離又は解離させてなる処理（プラズマ処理）が採用できる。

【0021】そして、前述の水酸基増加処理と併用して、前記被加工物を陽極とし、又は被加工物の電位を高く維持して、電界によって該被加工物の表面に水酸基イオンを引き寄せて、被加工物近傍の水酸基イオンの濃度を高めて加工することが実用的である。また、生成した OH^- と H^+ とが再結合して H_2O に戻るのを抑制するために、強電界をかけて被加工物に OH^- を引き寄せるか、水素吸蔵合金を用いるなどで H^+ イオンを強制的に除外する方法が有力である。

【0022】次に、各水酸基増加処理について説明する。まず、電解処理は、超純水中に間隔を置いて配設した一対又はそれ以上の電極間に電流を流し、超純水を電気分解してなる処理であるが、通常は陽極側を被加工物とした一対の電極を用い、両電極間に直流バイアス電圧を印加して行うのである。ここで、被加工物表面に単位時間に作用する OH^- を増加させるには、電極間の電界強度を増加させる、即ち電極間にかける直流バイアスを高くするか、電極間のギャップを小さくすれば良い。この場合、超純水中に存在するイオンは H^+ 、 OH^- のみ

であり、よって直流バイアスを印加した場合、陽極近傍には OH^- が多数存在することになる。この陽極近傍の OH^- によって、陽極となっている被加工物を加工するのである。被加工物の加工量は、一般にファラデーの法則によって決まり、被加工物の1グラム等量の元素を電解溶出させるのに必要な電気量は F （ファラデー定数）クーロンであり、電流密度が高い程、加工速度が速いことになる。

【0023】高温高圧処理は、超純水を高温、高圧に維持してなる処理であり、液体の状態では水のイオン積が圧力及び温度に依存してその絶対量が変化することを利用するものである。図1は、100 kbar（ 10^{10} Pa）、1000℃までの超高温、超高压領域において水の電気伝導度を測定することによって得られた水のイオン積 K_w と密度 ρ の関係のグラフである。尚、イオン積と pH との関係は、

$$\text{pH}(\text{H}_2\text{O}) = -\log[\text{H}^+] = -\log K_w^{1/2}$$
で与えられる。

【0024】イオン積と圧力、温度の関係の傾向は概ね以下のようなものである。まず、1～10 kbarの範囲で圧力一定の条件においては、イオン積は温度の上昇に伴い増加するが、その傾きは徐々に減少し、ある温度で極限値に達した後は温度の上昇に伴い減少する。30～100 kbarの範囲で圧力一定の条件においては、イオン積は単調増加する。次に、温度一定の条件においては、イオン積は圧力の増加に伴い増加する。また、密度一定の条件においても、イオン積は温度、圧力の上昇に伴い増加する。例えば、密度 1.0 g/cm^3 で室温（25℃）から200℃まで上昇させた場合、水のイオン積 K_w は 10^{-14} から約 $10^{-10.118}$ 程度に増加する一方で圧力は3 kbar（ 3×10^8 Pa、約3000気圧）に上昇する。

【0025】高温高圧・電解処理は、超純水を高温、高圧に維持しながら、超純水中に間隔を置いて配設した一対又はそれ以上の電極間に電流を流し、超純水を電気分解してなる処理であり、前述の電解処理と高温高圧処理とを組合せたものである。

【0026】イオン交換処理は、超純水中に配設したイオン交換機能を有する固体表面での電気化学反応を利用してなる処理であり、イオン交換樹脂膜又は透水性の仕切膜間にイオン交換樹脂粒若しくは固体電解質を充填したものなどを利用できる。そして、イオン交換機能を有する固体表面の両側に陽極と陰極を配設して、固体表面で生成した OH^- を陽極側に、 H^+ を陰極側に引き寄せて分離し、陽極として用いた被加工物又は陽極の近傍に配設した被加工物を OH^- によって加工するのである。また、触媒処理は、触媒機能を有する固体表面で水分子を励起若しくは活性化し、陽極と陰極間に印加した電圧によって水分子を電離若しくは解離させる処理である。

【0027】プラズマ処理は、超純水に誘電損失の可及

的小さな周波数の高周波電圧を印加して水プラズマを生成し、水を電離又は解離させてなる処理であり、典型的な非平衡状態で OH^- を生成する方法である。この場合、プラズマ中の OH^- を強電界をかけるなどで強制的に被加工物の加工面に作用させて加工するのである。また、水蒸気状態の超純水に高周波電圧を印加してプラズマを発生させることも考慮される。

【0028】ここで、本発明の加工原理は、超純水中の OH^- によって被加工物を加工するのであるが、加工が化学的溶出反応による除去加工であるか、あるいは酸化反応による酸化被膜形成加工であるかは、水酸基の供給量などの加工パラメーターを調節することによって選択することが可能である。しかし、この加工パラメーターは、水酸基増加処理の方法によっても異なり、現在のところ両加工を選択するための加工パラメーターの範囲は特定できない。

【0029】

【実施例】次に、実際に被加工物を加工した具体例に基づいて本発明を更に説明する。水酸基増加処理として、実施例1は電解処理、実施例2は高温高压処理、実施例3はイオン交換処理を採用し、被加工物としてSiを始め、その他の数種類の金属を用いて加工の実証試験を行った。

【0030】（実施例1-1）図2に示すように、陽極側をSi、陰極側を回転電極とした加工装置を用いて実証試験を行った。回転電極を使用する利点としては、電極間に一定な水の流れを作ること、安定した場での加工ができること、電極間に常に新しい水を供給すること、場を清浄に保つことができることなどが挙げられる。前者については、平板状の両電極が微小なギャップ（1mm以下）で対峙していると、両電極板の表面から発生した気泡がギャップ間に溜まってしまい、安定な場での加工が期待できないからである。この点について

は、従来の電解加工においても、電解液の流れを作って気泡を除去している。

【0031】本実施例の加工装置は、図2に示すように、Si板からなる試料1と、回転電極2とをギャップを設けて水槽3に満たした超純水4中に浸漬し、試料1はXYステージ5に固定されたサポート部材6に保持され、回転電極2はZステージ7に固定されたモータ8の回転軸9（Z軸方向）の先端に固定されている。前記試料1の加工面は、XY面と直交させて配設し、例えばYZ面と平行に配設している。従って、XYステージ5とZステージ7とを駆動することによって、試料1と回転電極2とのギャップ間隔を含め相対的位置を変更できるようになっている。そして、前記試料1と回転電極2は、それぞれ電源10にリード線11、11等を介して電氣的に接続され、試料1には正電圧が印加され、回転電極2は接地電位に維持されている。前記試料1と回転電極2との間に流れる電流は電流計12で測定している。また、前記水槽3を含め機構部分の殆どを気密チャンバー13内に収容し、該気密チャンバー13の内部はArガスでパージしている。

【0032】前記回転電極2の材料としては、 OH^- や H^+ によって侵されないものを用いる必要があり、AuやPtが最も好ましい。本実施例では、Al球の表面に無電解めっきによってNiを10 μm の厚さにコーティングし、その上に電解めっきによってAuをコーティングしたものを回転電極2として用いた。

【0033】先ず、両電極間（陽極の試料1と陰極の回転電極2との間）に印加する直流バイアスを一定にし、ギャップを変化させて電界強度を増加させてSiに作用する OH^- の量を増加させた場合のSiの変化の様子を観察した。加工条件及び加工結果を次の表1に示す。

【0034】

【表1】

実験 No.	加工条件				加工結果
	直流電圧 (V)	ギャップ (mm)	電流密度 (mA/cm ²)	時間 (hr)	
Nc.1	300	8	0.11	4	酸化（膜厚：0.05～0.12 μm ）
Nc.2	300	4	0.11	4	酸化（膜厚：0.06～0.1 μm ）
Nc.3	300	2	0.32	4	酸化（膜厚：0.08～0.1 μm ）
Nc.4	300	1	0.89	4	酸化（膜厚：0.4～0.5 μm ）

【0035】ここで、表1中の酸化膜の膜厚は、触針式粗さ計（（株）東京精密製、サーフコム）を用いて測定した。その結果、試料1に形成された酸化膜は、回転電極2が最も接近している中心部分が最も膜厚が厚く成長しており、中心から遠ざかるにつれて酸化膜の成長は小さくなっていった。これは、回転電極を用いたため、回転電極の中心から遠ざかるにつれてギャップが大きくなり、それに伴って電界強度が弱まった分布になってお

り、その結果としてSiに作用する OH^- の単位時間当たりの量が減少したためと推測される。上記の結果、少なくとも電流密度が0.9mA/cm²程度以下では、酸化被膜形成加工であることが分かる。

【0036】（実施例1-2）次に、電流密度を増加させるとともに、Siに作用する OH^- の濃度を一様にするために、平行平板電極を用いた加工を試みた。図3にその加工装置の概略を示している。この加工装置は、四

フッ化エチレン樹脂（PTFE）製の容器20に満たした超純水21中に、両極ともSi製の平板からなる試料22、22を絶縁体のスペーサ23を介して平行に固定した状態で浸漬し、一方の試料22に電源24から正電圧を印加し、他方の試料22を零電位に維持し、前記容器20の開口部は蓋25で覆った上にガス不透過性の袋26で密閉した構造を有し、その内部をArガスでパー

ジしている。尚、図中27は温度計である。

【0037】前述の実施例1-1と同様に、両試料22、22に直流バイアスを印加して、加工を試みた。その加工条件と加工結果を以下の表2に示し、この電流密度でも加工は酸化被膜形成加工であった。

【0038】

【表2】

実験 No.	加工条件				加工結果
	直流電圧 (kV)	ギャップ (mm)	電流密度 (mA/cm ²)	時間 (hr)	
No. 5	5	1	1.7	1	酸化（膜厚：0.15～0.2 μm）

【0039】（実施例1-3）次に、電流密度を更に増加させる目的で、陰極を針状の電極として加工を試みた。図4は、その加工装置の概略を示す。この加工装置は、密閉容器30内に配した水槽31に超純水32を満たし、保持台33に固定したSi製の平板からなる試料34を超純水32に浸漬するとともに、金線からなる針状電極35を該試料34に垂直に所定のギャップを設けて保持台33に固定して同様に超純水32中に浸漬し、電源36から試料34に正電圧を印加するとともに、針

状電極35を零電位に維持し、更に前記密閉容器30をArガスでパージする構造のものである。尚、図中37は温度計である。

【0040】前述の実施例1-1と同様に、両試料34と針状電極35間に直流バイアスを印加して、加工を試みた。その加工条件と加工結果を以下の表3に示し、この電流密度でも加工は酸化被膜形成加工であった。

【0041】

【表3】

実験 No.	加工条件				加工結果
	直流電圧 (kV)	ギャップ (mm)	電流密度 (mA/cm ²)	時間 (min)	
No. 6	10	1	7.9	10	酸化（膜厚：0.35 μm）

【0042】以上の結果より、被加工物がSiについては、電流密度が0.11～7.9 mA/cm²の範囲では、加工は酸化被膜形成加工であった。現在、半導体工業においてSi酸化膜は、ゲート絶縁膜やキャパシタ絶縁膜などSiデバイスの製造の様々な分野に利用されている。このSi酸化膜の生成法は様々あるが、今日のデバイス製造に用いられるSi酸化膜は、主としてSiを高温の雰囲気中に曝すことで均一に形成される熱酸化膜である。これまでSi酸化膜の生成法としては、乾燥酸化、加湿酸化、水蒸気酸化、加圧酸化、プラズマ酸化、電解陽極酸化などが知られている。

【0043】電解陽極酸化を除く他の方法では、酸化膜の特性はほぼ同様であるのに対し、電解陽極酸化による方法では酸化膜の密度は他の方法よりもかなり小さく、抵抗率も他の方法と比べて4桁も小さい。これは、電解陽極酸化法では、電解液中の電解質がSi酸化膜に大きく影響を与えるためと考えられる。本発明の加工方法で陽極に生じたSi酸化膜は、超純水中での陽極電極反応によるものである。そこで、本発明による酸化膜と熱酸

化膜とをFT-IR（Fourier Transfer-Infrared Spectroscopy）（日本分光製、FT/IR-3型）と、AES（Auger Electron Spectroscopy）によって分析した。FT-IRの分析結果からは、本発明の酸化膜は、一般にデバイス製造に用いられている熱酸化膜よりもSi-O結合の量が少ないことが分かった。しかし、一方ではAESの分析結果からは、本発明の酸化膜は熱酸化膜に匹敵する構造を持つということが分かった。従って、酸化被膜形成加工の加工条件を最適にすることにより、超純水中でSiの電極反応を行えば、熱酸化膜に匹敵するSi酸化膜が得られる可能性がある。

【0044】（実施例1-4）前述の実施例1-3の加工装置を使用し、試料としてCu、Mo、Fe、Alの加工を試みた。その加工条件と加工結果を以下の表4に示し、この加工条件ではCu、Moは除去加工、Fe、Alは酸化被膜形成加工であった。

【0045】

【表4】

被加工材料	加工条件				加工結果 (除去加工は比加工体積) (酸化加工は酸化膜厚)
	直流電圧 (kV)	ギャップ (mm)	電流密度 (mA/cm ²)	時間 (min)	
Cu	1~2	1	400	10	除去加工 (0.29mm ³ /A・min)
Mo	0.5	1	38	60	除去加工 (0.44mm ³ /A・min)
Fe	4.5	1	16	60	酸化 (膜厚: 18μm)
Al	6	1	12	60	酸化 (膜厚: 15μm)

【0046】ここで、加工終了直後に加工されたCu、Moの表面がそれぞれ茶褐色及び黒色に変化していた。これらは、Cuの酸化物CuO及びMoの酸化物MoO₃であると思われる。特に、Cuは加工中に緑色のもやが水中に現れ、またMoの加工終了後の水の一部に青色のもやがかかっていた。従って、加工されたCu及びMoの表面は酸化されていたと推測される。これらの結果から超純水中での電極反応による加工メカニズムの一つのモデルが考えられる。即ち、超純水中においては、物質は先ずOH⁻やH₂Oが関係することによって酸化が生じ、その酸化物が更にOH⁻やH₂Oが関係した何らかの原因で脱離することで除去加工に変わるというモデルである。

【0047】(実施例2)本実施例では、超純水を高温、高圧に維持して超純水中のOH⁻濃度を増大させ、超純水中に浸漬した被加工物を加工することを試みた。図1に示すように、室温付近の温度25℃で、大気圧における密度1.0g/cm³の水を、密度を一定にしたまま200℃まで温度を上昇させると圧力は3000気圧になることが分かる。そこで、本加工装置は、図5に示すように、圧力容器40の内部反応室41内に超純水42を満たした四フッ化エチレン樹脂製の容器43を配置し、超純水42中にSi製の試料44を浸漬し、また圧力容器40の外周には加熱用のセラミックヒーター4

5を巻回し、更にそれを断熱材46で覆った構造のものであり、セラミックヒーター45にはスライダック47を介して電流を供給するものである。尚、温度は圧力容器40に接触させた熱電対48で測定する。前記圧力容器40は、3000気圧に耐えるように設計されており、収容空間41を有する容器本体40aと蓋体40bを8本のボルト40cで締結し、容器本体40aと蓋体40bとは銅製のガスケット40dで密閉したものである。また、容器本体40aと蓋体40bとは、ステンレス鋼(SUS304)で作製し、ボルト40cは、線膨張率がステンレス鋼よりも小さいHPM2鋼で作製し、温度が上昇したときに、熱膨張率の違いによって締付力が増加する自緊構造となっている。

【0048】前記試料44としては、厚さ400μm、縦横の長さが1×2cmのSiウェハースを用いる。前処理として、先ずエチルアルコールでSiウェハース表面の油分やその他の汚れを拭き取り、次に5%フッ酸で30秒間洗浄して酸化膜の除去を行った。そして、最後に超純水(流水)中で10秒間洗浄を行い、十分に乾燥させた。加工前に、このSiウェハースの重量をmgオーダーで測定した。加工条件及び加工結果として加工前重量と加工後重量を次の表5に示している。

【0049】

【表5】

加工条件				加工結果		
水温	圧力	イオン積	時間	加工前重量	加工後重量	厚さ減少量
200℃	3000気圧	10.118	1hr	329mg	327mg	2.1μm

【0050】ここで、加工時間については、熱電対モニターが200℃を指示してから内部反応室中の超純水の温度が200℃になるまで待ち(10分間)、それから1時間の加工を行った。また、表中の厚さ減少量は、質量差/(密度×表面積)で計算した。

【0051】(実施例3)図6(a)及び(b)に示すような加工装置を用いてCu板の加工を試みた。この加工装置は、容器50内に満たした超純水51中に、陰極となる白金電極板52と陽極となるCu製の試料53を一定のギャップを保持して浸漬するとともに、両電極間に陽イオン交換膜(Nafion117)54を配設し、前記容器50の全体を気密容器55内に収容して、その内部をA

rガスでパージする構造である。更に詳しくは、内部を開口したギャップスペーサー56の側面側に前記陽イオン交換膜54を挟んで白金電極板52を固定し、ギャップスペーサー56の他側面側に前記試料53を固定し、この状態で超純水51中に浸漬する。この場合、ギャップスペーサー56の開口56aの内部にも超純水51が満たされる。そして、電源57から前記白金電極板52と試料53間に、加工中に電流値が一定となるように直流電圧を印加した。加工条件と加工結果を次の表6に示す。

【0052】

【表6】

	加工条件			加工結果
	対向面積	ギャップ	電流値	比加工体積
加工1	1×4.5(cm ²)	2mm	40mA	2.35 mm ³ /A・min
加工2	1×3 (cm ²)	2mm	30mA	0.83 mm ³ /A・min

【0053】ここで、表6中の加工1においては、陽イオン交換膜を乾燥したまま超純水に浸漬して加工を行った結果、陽イオン交換膜を加工終了後に観察すると、陽イオン交換膜は超純水との接触部だけが水を吸収して試料側に膨張していた。その結果、陽イオン交換膜と試料とのギャップは殆どなかった。それに対して、表6中の加工2においては、陽イオン交換膜を予め超純水に十分な時間浸漬して膜の膨張を一樣にした後、更に超純水で十分に洗浄した後にギャップスペーサーにセッティングした。その結果、加工1では40mAの電流値を確保するために印加した電圧は数10Vであったのに対し、加工2では30mAの電流値を確保するために印加した電圧は600～1400Vになった。

【0054】このイオン交換処理によってOH⁻濃度を増加させる加工方法では、イオン交換材を表面に有する特定形状の工具を陰極とし、被加工物を陽極として加工をすれば、工具の形状を被加工物に転写する加工（転写加工）や、イオン交換材を表面に有するワイヤー電極を陰極として用いれば、陽極の被加工物を切断する加工（切断加工）が可能である。

【0055】

【発明の効果】以上にしてなる本発明の超純水中の水酸基による加工方法によれば、以下の顕著な効果を奏する。

- ①OH⁻イオンと被加工物の化学的作用による加工であるため、被加工物の特性を損なうことはない。
- ②電解加工等で使用する水溶液と違い超純水中にはH⁺、OH⁻及びH₂Oのみが存在し、金属イオン等の不純物は存在しないので、外部からの不純物の遮断が完全であれば、完全に清浄な雰囲気中での加工が可能である。
- ③超純水のみを使用するため加工コストの大幅な低減も可能である。

【図面の簡単な説明】

【図1】温度と圧力をパラメータとした水の密度とイオン積との関係を示すグラフである。

【図2】水酸基増加処理として電解処理を採用し、回転電極を用いた加工装置の簡略断面図である。

【図3】水酸基増加処理として電解処理を採用し、平行平板電極を用いた加工装置の簡略断面図である。

【図4】水酸基増加処理として電解処理を採用し、針状電極を用いた加工装置の簡略断面図である。

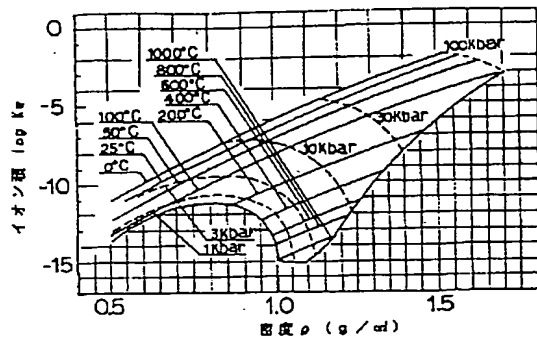
【図5】水酸基増加処理として高温高圧処理を採用した加工装置の簡略断面図である。

【図6】水酸基増加処理としてイオン交換処理を採用した加工装置を示し、(a)は装置の簡略断面図、(b)は電極周辺構造を示す分解斜視図である。

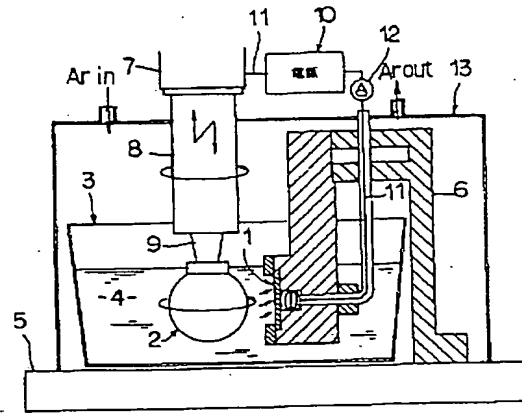
【符号の説明】

- | | |
|--------------|-------------|
| 1 試料（被加工物） | 2 回転電極 |
| 3 水槽 | 4 超純水 |
| 5 XYステージ | 6 サポート部材 |
| 7 Zステージ | 8 モータ |
| 9 回転軸 | 10 電源 |
| 11 リード線 | 12 電流計 |
| 13 気密チャンバー | |
| 20 容器 | 21 超純水 |
| 22 試料（被加工物） | 23 スペーサ |
| 24 電源 | 25 蓋 |
| 26 袋 | 27 温度計 |
| 30 密閉容器 | 31 水槽 |
| 32 超純水 | 33 保持台 |
| 34 試料（被加工物） | 35 針状電極 |
| 36 電源 | 37 温度計 |
| 40 圧力容器 | |
| 40a 容器本体 | 40b 蓋体 |
| 40c ボルト | 40d ガスケット |
| 41 内部反応室 | 42 超純水 |
| 43 容器 | 44 試料（被加工物） |
| 45 セラミックヒーター | 46 断熱材 |
| 47 スライダック | 48 熱電対 |
| 50 容器 | 51 超純水 |
| 52 白金電極板 | 53 試料（被加工物） |
| 54 陽イオン交換膜 | 55 気密容器 |
| 56 ギャップスペーサー | |
| 56a 開口 | |
| 57 電源 | |

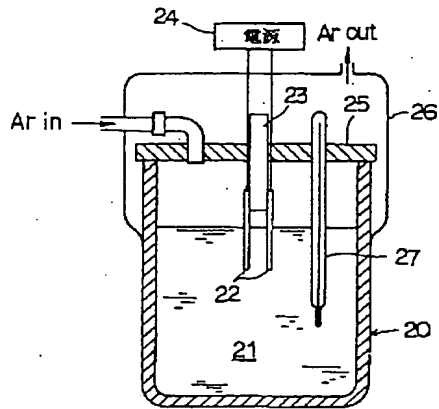
【図 1】



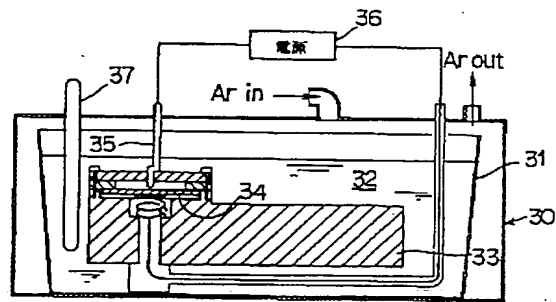
【図 2】



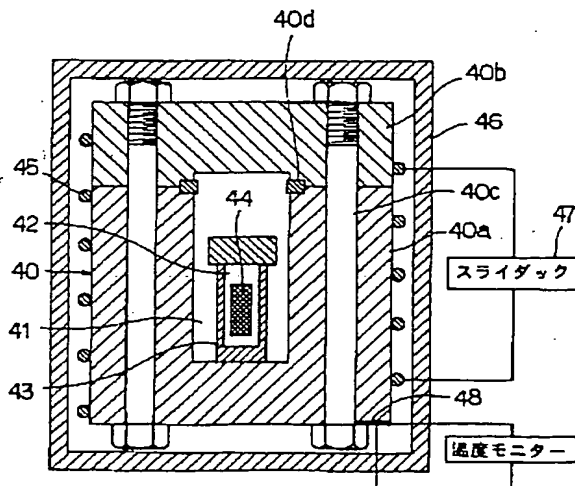
【図 3】



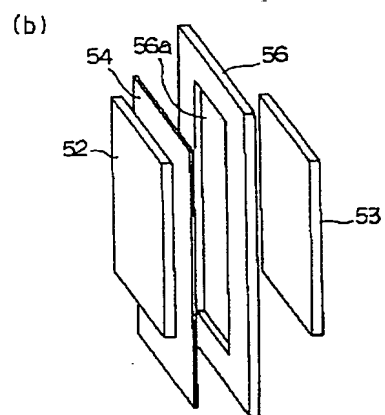
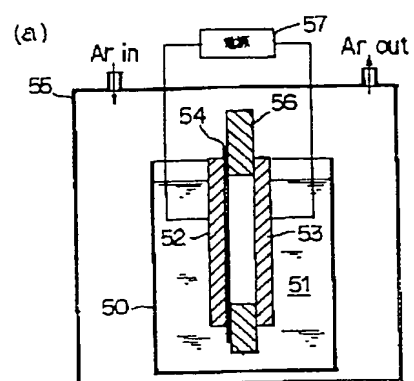
【図 4】



【図 5】



【図 6】



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JAPANESE PATENT OFFICE

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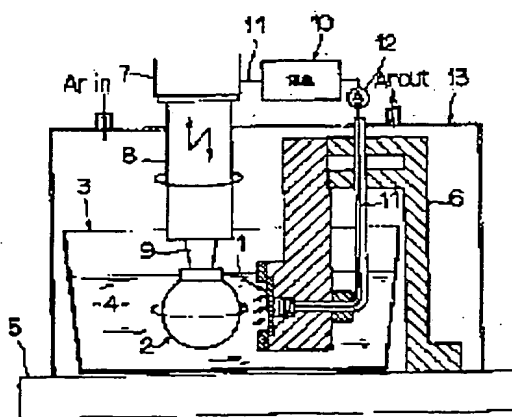
MORI YUZO

(54) MACHINING METHOD USING HYDROXYL GROUP IN ULTRAPURE WATER

(57)Abstract:

PROBLEM TO BE SOLVED: To purely machine a workpiece without leaving impurities on the machining surface thereof by removing the impurities, or forming an oxidized coat through a chemical elution reaction or oxidizing reaction process using a hydroxyl group or hydroxyl group ions.

SOLUTION: Water molecules in ultrapure water 4 are ionized and a hydroxyl group or hydroxyl group ions so generated are supplied to the surface of a workpiece 1. A pure oxidized film is formed on material surface via the reaction of workpiece atoms with the hydroxyl group or hydroxyl group ions, or material surface atoms are removed and a desired shape is obtained through the repetition of the process. When the hydroxyl group or hydroxyl group ions as machining aids are generated via chemical reaction on the surface of an electrode 2 positioned



near the surface of the workpiece 1 or on the surface of a solid having an ion exchange function or a catalytic function, workpiece surface in the vicinity of the surface of a solid generating such a hydroxyl group or ions is preferentially machined. Thus, the shape of a material generating the hydroxyl group or hydroxyl group ion is transcribed on the surface of the workpiece 1.

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Application Date: August 12, 1996

Request for Examination: Not made

Inventor: Yuzo Mori

Applicant: Yuzo Mori

Title of the Invention:

MACHINING METHOD BY HYDROXYL GROUP IN ULTRAPURE
WATER

[Abstract]

[Problem] To provide a completely new machining method by hydroxyl group in ultrapure water, which can perform a clean machining without leaving impurities in a machined surface of a workpiece by using OH^- in the ultrapure water on the basis of a recognition that, if an OH^- concentration in the ultrapure water is increased, the machining can be sufficiently performed by utilizing OH^- .

[Mean for Resolution] Only an ultrapure water except slight amounts of unavoidable impurities is used, to this a hydroxyl group increase treatment for increasing an ion product is applied, and a workpiece immersed in the ultrapure water whose concentration of

the hydroxyl group or hydroxyl group ions has been increased is subjected to a removal machining or an oxide film formation machining by means of a chemical elusion reaction or an oxidation reaction by the hydroxyl group or the hydroxyl group ions.

[Claims]

[Claim 1] A machining method by hydroxyl group in ultrapure water, characterized in that only an ultrapure water except slight amounts of unavoidable impurities is used, to this a hydroxyl group increase treatment for increasing an ion product is applied, and a workpiece immersed in the ultrapure water whose concentration of the hydroxyl group or hydroxyl group ions has been increased is subjected to a removal machining or an oxide film formation machining by means of a chemical elusion reaction or an oxidation reaction by the hydroxyl group or the hydroxyl group ions.

[Claim 2] A machining method by hydroxyl group in ultrapure water set forth in claim 1, wherein, as the hydroxyl group increase treatment, an electric current is flowed between one pair or more of electrodes arranged in the ultrapure water with an interval being provided between them to thereby electrolyze the ultrapure water.

[Claim 3] A machining method by hydroxyl group in ultrapure water set forth in claim 1, wherein, as the hydroxyl group increase treatment, the ultrapure water is maintained at a high temperature and under a high pressure.

[Claim 4] A machining method by hydroxyl group in ultrapure water set forth in claim 1, wherein, as the hydroxyl group increase treatment, while maintaining the ultrapure water at a high temperature and under a high pressure an electric current is flowed between one pair or more of electrodes arranged in the ultrapure water with an interval being provided between them to thereby electrolyze the ultrapure water.

[Claim 5] A machining method by hydroxyl group in ultrapure water set forth in claim 1, wherein, as the hydroxyl group increase treatment, an electrochemical reaction on a solid surface arranged in the ultrapure water and having an ion exchange function or a catalyst function is utilized.

[Claim 6] A machining method by hydroxyl group in ultrapure water set forth in claim 1, wherein, as the hydroxyl group increase treatment, a water plasma is generated by applying a high frequency voltage of frequency whose dielectric loss is as small as possible

to the ultrapure water to thereby ionize or dissociate the water.

[Claim 7] A machining method by hydroxyl group in ultrapure water set forth in any of claims 1 to 6, wherein the workpiece is made an anode or an electric potential of the workpiece is maintained high to thereby attract the hydroxyl group ions to a surface of the workpiece.

[Detailed Description of the Invention]

[0001]

[Technical Field to which the Invention Belongs] The present invention concerns a machining method by hydroxyl group in ultrapure water and, more detailedly, relates to a machining method in which only an ultrapure water is used, its ion product is increased and a workpiece can be subjected to a removal machining or an oxide film formation machining by hydroxyl group or hydroxyl group ions.

[0002]

[Prior Art] In recent years, under a development of technology, the development in new materials is advancing in succession, but a machining technique effective for these materials has not been established yet, so that it is in a standpoint running always after them.

[0003] Further, recently, as a constituent element of all equipments is made finely and with a high accuracy and an article manufacture in submicron region becomes general, an influence of a machining method itself exerting on properties of the material becomes increasingly large. Under such a situation, with a machining method in which a workpiece is removed by a tool while being physically destroyed like a conventional machining, since many defects are generated in the workpiece by the machining, the properties of the workpiece are deteriorated. Accordingly, how the working can be performed without deteriorating the properties of the material becomes a problem.

[0004] In special machining methods first developed as means for solving this problem, there are a chemical polishing, an electrolytic machining and an electrolytic polishing. In contrast to the conventional physical machining, these machining methods perform a removal machining by generating a chemical elusion reaction. Accordingly, defects such as machined alteration layer and dislocation etc. by a plastic deformation don't occur, so that the aforesaid problem of performing the machining without deteriorating the properties of the material is

solved.

[0005]And, a machining method utilizing a chemical interaction between atoms is further noted. This is one utilizing fine particles and radicals etc. having a high chemical reactivity. In these machining methods, since the removal machining is performed in atom order by a chemical reaction with the workpiece, a machining control in atom order is possible. As examples of this machining method, there are an EEM (Elastic Emission Machining) (Japanese Patent Laid-Open No. 236939/1989 Gazette) and a plasma CVM (Chemical Vaporization Machining) (Japanese Patent Laid-Open No. 125829/1989 Gazette etc.), which were developed by the present inventor. The EEM is one utilizing a chemical reaction between the fine particles and the workpiece, and realizes the machining in atom order without deteriorating the properties of the material. Further, the plasma CVM is one utilizing a radical reaction between the radical generated in an atmospheric pressure plasma and the workpiece, and realizes the machining in atom order.

[0006]

[Problems that the Invention is to Solve] By the way, it is hitherto construed that, in the aforesaid

electrolytic machining and electrolytic polishing, the machining proceeds by an electrochemical interaction between the workpiece and an electrolysis solution (aqueous solution of NaCl, NaNO₃, HF, HCl, HNO₃, NaOH, and the like). Further, so long as the electrolysis solution is used, it is unavoidable that the workpiece is contaminated by that electrolysis solution.

[0007] Therefore, the inventor has considered that, in the neutral and alkaline electrolysis solutions, a hydroxyl group (OH⁻) acts on the machining, and has reached an assumption that, if this is true, the machining can be performed also by a water in which OH⁻ exists even though in slight amount. If the machining can be performed by utilizing OH⁻ in the ultrapure water, a clean machining can be performed without leaving impurities on a machined surface, so that it is considered that its use is very wide besides a semiconductor manufacture field. However, it is a well known fact that an OH⁻ concentration contained in the ultrapure water is very dilute and in the order of 10⁻⁷ mol/l at 25°C under 1 atm, and until now there is no report of such a content that an etching is performed by immersing Si in the ultrapure water for instance.

[0008] A problem that the invention is to solve in

view of the situation mentioned above is to provide a completely new machining method by hydroxyl group in ultrapure water, which can perform a clean machining without leaving impurities in a machined surface of a workpiece by using OH^- in the ultrapure water on the basis of a recognition that, if an OH^- concentration in the ultrapure water is increased, the machining can be sufficiently performed by utilizing OH^- .

[0009]

[Means for Solving the Problems] In order to solve the aforesaid problem, the invention provides a machining method by hydroxyl group in ultrapure water, characterized in that only an ultrapure water except slight amounts of unavoidable impurities is used, to this a hydroxyl group increase treatment for increasing an ion product is applied, and a workpiece immersed in the ultrapure water whose concentration of the hydroxyl group or hydroxyl group ions has been increased is subjected to a removal machining or an oxide film formation machining by means of a chemical elusion reaction or an oxidation reaction by the hydroxyl group or the hydroxyl group ions.

[0010] Here, as the hydroxyl group increase treatment, there is adopted the fact that an electric current is flowed between one pair or more of electrodes

arranged in the ultrapure water with an interval being provided between them to thereby electrolyze the ultrapure water, or the fact the ultrapure water is maintained at a high temperature and under a high pressure, or the fact that while maintaining the ultrapure water at the high temperature and under the high pressure the electric current is flowed between one pair or more of electrodes arranged in the ultrapure water with the interval being provided between them to thereby electrolyze the ultrapure water, or the fact that an electrochemical reaction on a solid surface arranged in the ultrapure water and having an ion exchange function or a catalyst function is utilized, or the fact that a water plasma is generated by applying a high frequency voltage of frequency whose dielectric loss is as small as possible to the ultrapure water to thereby ionize or dissociate the water.

[0011] And, it is most preferable that, by using the hydroxyl increase treatment in combination, the machining is performed by means of increasing a concentration of the hydroxyl group in the vicinity of the workpiece by making the workpiece an anode or maintaining an electric potential of the workpiece high to thereby attract hydroxyl group ions to a

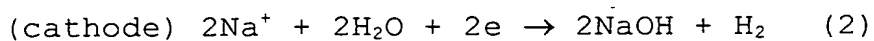
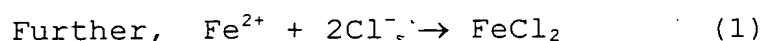
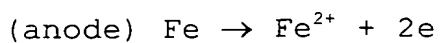
surface of the workpiece.

[0012]

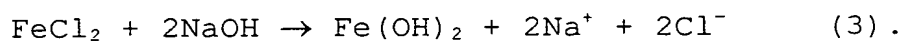
[Mode for Carrying Out the Invention] An origin of the machining method, for various materials, of the invention utilizing the ultrapure water exists in a question about a reaction mechanism in the conventional electrolytic machining. The electrolytic machining is a machining method for obtaining desired shape, dimension and surface state by concentrating and limiting an electrochemical dissolution action (anode elusion or electrolytic elusion) to a desired portion of the material. Concretely, it is one in which the machining is performed by opposing in the electrolysis solution a cathode made in a desired shape to an anode that is the workpiece with a gap of 0.02 to 0.7 mm being provided between them and applying a DC voltage of 5 to 20 V (current density is 30 to 200 A/cm²). By these conditions, by means of generating the electrolytic elusion while concentrating and limiting it to a very vicinity of the anode, the workpiece is machined to a shape in which the shape of the cathode that is a tool is inverted.

[0013] Next, an established theory of the reaction mechanism in the conventional electrolytic machining

is explained briefly. For example, in case where the electrolytic machining of Fe is performed by using an NaCl aqueous solution as the electrolysis solution, it is generally construed that a reaction process in its both electrodes becomes as follows.



In this manner, FeCl_2 generated in the cathode reacts with NaOH generated in the anode in the ultrapure water and becomes



Thus, if the equations (1) to (3) are added in their members, the above reaction equation becomes

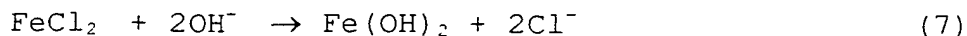


[0014] Therefore, the equation (3) is made a question and, in this equation, it seems that NaOH reacts with FeCl_2 in a form as it is. However, as to NaOH, since Na is high in its ionization tendency, it is considered that, in the electrolysis solution, NaOH is ionized to Na^+ and OH^- like a following equation (5).

That is, it becomes + H_2



If this process is taken into consideration, the equation (2) and the equation (3) become respectively



and if the equation (1), the equation (6) and the equation (7) are added in their members, the equation (4) is conducted similarly.

[0015] If both of the reaction process of the equation (1) to the equation (3) and the reaction process of the equation (1) \rightarrow the equation (6) \rightarrow the equation (7) are compared, it is understood that NaOH itself contributes to the reaction in both, while OH^- generated by the fact that NaOH is ionized contributes to the reaction in the latter. That is, in the latter it is considered that, if OH^- exists, the reaction proceeds. Here, OH^- exists not only in the solution but also in a water of merely pure water although in a slight amount (10^{-7} mol/l at 25°C). Accordingly, basing on the aforesaid thought, it follows that the machining of the material similar to in a alkaline solution is possible by utilizing OH^- in the ultrapure water.

[0016] However, as mentioned above, since OH^- in the ultrapure water is a slight amount, in order to make a practical machining possible, an OH^- concentration must be increased by some method. In the invention, the machining of the material in an extremely cleaned

environment is performed by increasing the OH^- concentration in the ultrapure water without adding another solution. Accordingly, in the machining of the invention, a contamination of the workpiece surface does not occurs.

[0017] A machining principle of the invention is one in which water molecules in the ultrapure water are ionized, generated hydroxyl group or hydroxyl group ions is/are supplied to the workpiece surface, a clean oxide film is formed on the material surface or material surface atoms are removed by a reaction between the workpiece atoms and the hydroxyl group or the hydroxyl group ions, and by its accumulation an aimed shape is obtained.

[0018] In other words, if the hydroxyl group or the hydroxyl group ions becoming a machining tool is/are generated by a chemical reaction on an electrode surface installed in the vicinity of the workpiece surface or a solid surface having the ion exchange function or the catalyst function, the workpiece surface in the vicinity of the solid material surface generating such hydroxyl group or hydroxyl group ions is preferentially machined. Accordingly, a so-called transcription machining in which a shape of the material generating the hydroxyl group or the hydroxyl

group ions is transcribed to the workpiece surface is possible. Further, in case where the shape of the material generating the hydroxyl group or the hydroxyl group ions is linear, a cut machining of plate-like material is possible. And, by adjusting machining parameters such as supply amount of the hydroxyl group or the hydroxyl group ions, it is possible to select whether the reaction induced on the material surface is an oxidation reaction or a removal machining reaction.

[0019] In the machining method of the invention, in order to increase a machining speed (machining efficiency), the hydroxyl group increase treatment is important. As to the hydroxyl group increase treatment, there are a method of increasing OH^- under a thermal equilibrium state, and a method of increasing OH^- under a thermal nonequilibrium state (utilizing no thermal equilibrium). If the hydroxyl group increase treatment is seen from a viewpoint of the machining, in order to limit a machining region by locally concentrating OH^- , it is preferable to increase OH^- by the method not utilizing the thermal equilibrium. However, even if OH^- is increased under the thermal equilibrium state, if only OH^- can be separated or accumulated and supplied to the machined

surface of the workpiece, it is possible to similarly limit the machining region.

[0020] As the hydroxyl group increase treatment, there can be adopted a treatment (electrolytic treatment) in which an electric current is flowed between one pair or more of electrodes arranged in the ultrapure water with an interval being provided between them to thereby electrolyze the ultrapure water, or a treatment (high temperature and high pressure treatment) in which the ultrapure water is maintained at a high temperature and under a high pressure, or a treatment (high temperature and high pressure / electrolytic treatment) in which while maintaining the ultrapure water at the high temperature and under the high pressure the electric current is flowed between one pair or more of electrodes arranged in the ultrapure water with the interval being provided between them to thereby electrolyze the ultrapure water, or a treatment (ion exchange treatment) in which an electrochemical reaction on a solid surface arranged in the ultrapure water and having an ion exchange function is utilized, or a treatment (catalyst treatment) in which a reaction on a solid surface arranged in the ultrapure water and having a catalyst function is utilized, or a treatment (plasma

treatment) in which a water plasma is generated by applying a high frequency voltage of frequency whose dielectric loss is as small as possible to the ultrapure water to thereby ionize or dissociate the water.

[0021] And, it is practical that, by using the hydroxyl increase treatment in combination, the machining is performed by means of increasing a concentration of the hydroxyl group in the vicinity of the workpiece by making the workpiece an anode or maintaining an electric potential of the workpiece high to thereby attract hydroxyl group ions to a surface of the workpiece by an electric field. Further, in order to suppress generated OH^- and H^+ from connecting again to return to H_2O , a method of attracting OH^- to the workpiece by applying a strong electric field or a method of forcibly eliminating H^+ ions by such a means as using hydrogen absorbing alloys is effective.

[0022] Next, it is explained about each hydroxyl group increase treatment. First, although the electrolytic treatment is a treatment in which an electric current is flowed between one pair or more of electrodes arranged in the ultrapure water with an interval being provided between them to thereby electrolyze the

ultrapure water, generally it is performed by using one pair of electrodes in which an anode side is made the workpiece, and applying a DC bias voltage between both electrodes. Here, in order to increase OH^- acting on the workpiece surface per unit time, it suffices if an electric field intensity between the electrodes is increased, i.e., the DC bias applied between the electrodes is raised, or a gap between the electrodes is reduced. In this case, ions existing in the ultrapure water are only OH^- and H^+ , so that in case where the DC bias is applied it follows that many OH^- exist in the vicinity of the anode. By these OH^- in the vicinity of the anode, the workpiece having become an anode is machined. A machined amount of the workpiece is generally determined by Faraday's law, and a quantity of electricity necessary for electrolytically eluting 1 gram equivalent of elements of the workpiece is F (Faraday constant) coulomb, so that it follows that the higher a current density is, the higher is a machining speed.

[0023] The high temperature and high pressure treatment is a treatment in which the ultrapure water is maintained at a high temperature and under a high pressure, and one utilizing the fact that under a liquid state an ion product of the water changes in

its absolute quantity in dependence of the temperature and the pressure. Fig.1 is a graph of a relation between the ion product K_w and a density ρ , which has been obtained by measuring an electric conductivity of the water in an ultra high temperature and ultra high pressure region up to 1000°C and 100 kbar (10^{10} Pa). Incidentally, a relation between the ion product and pH is given by

$$\text{pH (H}_2\text{O)} = -\log [\text{H}^+] = -\log K_w^{1/2}.$$

[0024] A tendency of the reaction between the ion product, the pressure and the temperature is generally as follows. First, under a condition that the pressure is constant in a range of 1 to 10 kbar, the ion product increases with a rise of the temperature, but its gradient reduces gradually, and after reaching a limit value at a certain temperature it reduces with the rise of the temperature. Under a condition that the pressure is constant in a range of 30 to 100 kbar, the ion product monotonously increases. Next, under a constant temperature condition, the ion product increases with a rise of the pressure. Further, also under a constant density condition, the ion product increases with rises of the temperature and the pressure. For example, in case where the density is 1.0 g/cm^3 and the temperature is raised from a room

temperature (25°C) to 200°C, the ion product K_w of the water increases to a degree of 10^{-14} to about $10^{-10.118}$, while the pressure rises to 3 kbar (3×10^8 Pa, about 3000 atm).

[0025] The high temperature and high pressure / electrolytic treatment is a treatment in which while maintaining the ultrapure water at the high temperature and under the high pressure the electric current is flowed between one pair or more of electrodes arranged in the ultrapure water with the interval being provided between them to thereby electrolyze the ultrapure water, and one in which the aforesaid electrolytic treatment and high temperature and high pressure treatment are combined.

[0026] The ion exchange treatment is a treatment in which an electrochemical reaction on a solid surface arranged in the ultrapure water and having an ion exchange function is utilized, and can utilize one in which ion exchange resin particles or a solid electrolyte are/is filled between ion exchange resin membranes or between water permeable partition membranes, and the like. And, it performs the machining by means of arranging the anode and the cathode on both sides of the solid surface having the ion exchange function, attracting OH^- generated on the

solid surface to an anode side and H^+ to a cathode side to thereby separate them, and machining the workpiece used as the anode or the workpiece arranged in the vicinity of the anode by OH^- . Further, the catalyst treatment is a treatment in which water molecules are excited or activated on the solid surface having a catalyst function; and the water molecules are ionized or dissociated by a voltage applied between the anode and the cathode.

[0027] The plasma treatment is a treatment in which a water plasma is generated by applying a high frequency voltage of frequency whose dielectric loss is as small as possible to the ultrapure water to thereby ionize or dissociate the water, and is a typical method of generating OH^- under the nonequilibrium state. In this case, the machining is performed by means of forcibly causing OH^- in the plasma to act on the machined surface of the workpiece by such a means as applying a strong electric field. Further, it is considered to generate the plasma by applying the high frequency voltage to the ultrapure water of a water vapor state.

[0028] Here, although the machining principle of the invention machines the workpiece by OH^- in the ultrapure water, whether the machining is the removal machining by the chemical elution reaction or the

oxide film formation machining by the oxidation reaction can be selected by adjusting machining parameters such as supply amount of the hydroxyl group. However, the parameters are different also in dependence of a method of the hydroxyl increase treatment, so that ranges of the machining parameters for selecting both machinings are not specified at present.

[0029]

[Embodiments] Next, on the basis of concrete examples in which the workpiece is actually machined, the invention is further explained. As the hydroxyl group increase treatment, an Embodiment 1 adopts the electrolytic treatment, an Embodiment 2 the high temperature and high pressure treatment and an Embodiment 3 the ion exchange treatment, and demonstration tests of the machining were performed by using, besides Si, other several kinds of metals as the workpiece.

[0030] (Embodiment 1-1) As shown in Fig.2, the demonstration test was performed by using a machining apparatus in which Si was made an anode side and a rotary electrode a cathode side. As advantages of using the rotary electrode, there are enumerated the facts that the machining in a stabilized field can be

performed owing to the fact that a constant water flow is generated between the electrodes, the field can be kept clean owing to the fact that a fresh water is always supplied between the electrodes, and the like. The former is because, if both electrodes of flat plate form are facing with a minute gap (1 mm or less) being provided between them, bubbles generated from surfaces of both electrodes stagnate in the gap, so that the machining in the stable field cannot be expected. As to this point, also in a conventional electrolytic machining, the bubbles are removed by making a flow of the electrolysis solution.

[0031] As shown in Fig.2, in the machining apparatus of this embodiment, a sample 1 consisting of Si plate and a rotary electrode 2 are immersed with a gap being provided between them in an ultrapure water 4 filled in a water tank 3, the sample 1 is held by a support member 6 fixed to an XY stage 5, and the rotary electrode 2 is fixed to a tip of a rotation shaft 9 (Z axis direction) of a motor 8 fixed to a Z stage 7. A machined face of the sample 1 is arranged orthogonally to an XY face and, for example, arranged parallel to a YZ face. Accordingly, it is adapted such that, by driving the XY stage 5 and the Z stage 7, a relative position including a gap interval between the sample 1

and the rotary electrode 2 can be changed. And, the sample 1 and the rotary electrode 2 are electrically connected respectively to an electric source 10 through lead wires 11, 11 etc., a positive voltage is applied to the sample 1, and the rotary electrode 2 is maintained at an earth electric potential. An electric current flowing between the sample 1 and the rotary electrode 2 is being measured by an ammeter 12. Further, most of a mechanism portions including the water tank 3 is accommodated in a gas tight chamber 13, and an inside of the gas tight chamber 13 is purged by Ar gas.

[0032] As a material of the rotary electrode 2, it is necessary to use one not eroded by OH^- and H^+ , and Au and Pt are most preferable. In this embodiment, as the rotary electrode 2 there was used one in which Ni was coated in a thickness of 10 μm on a surface of an Al sphere by an electroless plating and thereon Au was coated by an electrolytic plating.

[0033] First, there was observed an aspect in change of Si in case where a DC bias applied between both electrodes (the sample 1 of anode and the rotary electrode 2 of cathode) was made constant, and the gap was changed to increase an electric field intensity, thereby increasing a quantity of OH^- acting on Si.

Machining conditions and machined results are shown in Table 1 below.

[0034]

[Table 1]

Experiment	Machining conditions				Machined results
	DC voltage (V)	Gap (mm)	Current density (mA/cm ²)	Time (hr)	
No.1	300	8	0.11	4	Oxidation (Film thickness : 0.05~0.12 μ m)
No.2	300	4	0.11	4	Oxidation (Film thickness : 0.06~0.1 μ m)
No.3	300	2	0.32	4	Oxidation (Film thickness : 0.08~0.1 μ m)
No.4	300	1	0.89	4	Oxidation (Film thickness : 0.4~0.5 μ m)

[0035] Here, a film thickness of the oxide film in Table 1 was measured by using a stylus type roughnessmeter (Surfcom made by Tokyo Seimitsu Co., Ltd.). As a result, as to the oxide film formed on the sample 1, the film thickness grew thickest in a center portion where the rotary electrode 2 approached nearest, and the growth of the oxide film became small as going away from the center. It is inferred that this is attributable to the fact that, since the rotary electrode was used, the gap became large as going away from the center of the rotary electrode and, accompanying it, the electric field intensity became a weakened distribution and, as a result, the quantity of OH⁻ acting on Si per unit time was reduced. From the above results, it is understood that, if at least the current density is lower than

about 0.9 mA/cm², the machining is an oxide film formation machining.

[0036] (Embodiment 1-2) Next, in order to increase the current density and homogenize the concentration of OH⁻ acting on Si, a machining using parallel flat plate electrodes was attempted. An outline of its machining apparatus is shown in Fig.3. This machining apparatus has a structure in which samples 22, 22 of both electrodes each consisting of a flat plate made of Si are immersed in an ultrapure water 21 filled in a container 20 made of tetrafluoroethylene resin (PTFE) under a state that they are parallel fixed through a spacer 23 of insulator, a positive voltage is applied to one sample 22 from an electric source 24, the other sample 22 is maintained at a zero electric potential, and an opening portion of the container 20 is covered with a lid 25 and, additionally, sealed by a gas impermeable bag 26, and its inside is purged by Ar gas. Incidentally, 27 in the drawing is a thermometer.

[0037] Similarly to the aforesaid Embodiment 1-1, the DC bias was applied to both samples 22, 22, and a machining was attempted. Its machining conditions and a machined result are shown in Table 2 below. Also with this current density, the machining was the oxide

film formation machining.

[0038]

[Table 2]

Experiment	Machining conditions				Machined result
	DC voltage (kV)	Gap (mm)	Current density (mA/cm ²)	Time (hr)	
No.5	5	1	1.7	1	Oxidation (Film thickness : 0.15~0.2 μ m)

[0039] (Embodiment 1-3) Next, for the purpose of further increasing the current density, a machining was attempted with the cathode being made a needle-like electrode. Fig.4 shows an outline of its machining apparatus. This machining apparatus is of a structure in which an ultrapure water 32 is filled in a water tank 31 arranged in a sealed container 30, a sample 34 consisting of a flat plate made of Si and fixed to a holding base 33 is immersed in the ultrapure water 32, a needle-like electrode 35 consisting of a gold wire is fixed to the holding base 33 vertically to the sample 34 with a predetermined gap being provided between them and is similarly immersed in the ultrapure water 32, a positive voltage is applied to the sample 34 from an electric source 36, the needle-like electrode 35 is maintained at a zero electric potential and, further, the sealed container 30 is purged by Ar gas. Incidentally, 37 in the drawing is a thermometer.

[0040] Similarly to the aforesaid Embodiment 1-1, the DC bias was applied between the sample 34 and the needle-like electrode 35, and a machining was attempted. Its machining conditions and a machined result are shown in Table 3 below. Also with this current density, the machining was the oxide film formation machining.

[0041]

[Table 3]

Experiment	Machining conditions				Machined result
	DC voltage (kV)	Gap (mm)	Current density (mA/cm ²)	Time (min)	
No.6	10	1	7.9	10	Oxidation (Film thickness : 0.35 μ m)

[0042] From the above results, in regard to the workpiece of Si, in a range in which the current density is 0.11 to 7.9 mA/cm² the machining was the oxide film formation machining. At present, in the semiconductor industry, a Si oxide film is utilized in various fields of manufacturing Si devices such as gate insulation film and capacitor insulation film. Although there are various methods for generating this Si oxide film, the Si oxide film used in nowadays device manufacture is a heat oxide film uniformly formed by exposing Si mainly to a high temperature atmosphere. Hitherto, as methods of generating the Si oxide film, there have been known a dry oxidation, a

humidification oxidation, a water vapor oxidation, a pressurized oxidation, a plasma oxidation, an electrolytic anode oxidation, and the like.

[0043] In the other methods excluding the electrolytic anode oxidation, properties of the oxide film are approximately similar, whereas in a method by the electrolytic anode oxidation a density of the oxide film is considerably lower than the other methods and also a resistivity is lower even by four digits in comparison with the other methods. It is considered that this is because, in the electrolytic anode oxidation method, the Si oxide film is greatly influenced by the electrolyte in the electrolysis solution. The Si oxide film generated in the anode by the machining method of the invention is one owing to an anode electrode reaction in the ultrapure water. Therefore, the oxide film according to the invention and the heat oxidation film were analyzed by an FT-IR (Fourier Transfer - Infrared Spectroscopy) (FT/IR - 3 Type made by Nihon Bunko) and an AES (Auger Electron Spectroscopy). From results of the FT-IR, it was understood that, as to the oxide film of the invention, a quantity of Si-O bonds was less than the heat oxidation film generally used in the device manufacture. However, on the other hand, from results

of the AES, it was understood that the oxide film of the invention had a structure comparable to the heat oxide film. Accordingly, if the electrode reaction of Si in the ultrapure water is performed by optimizing the machining conditions of the oxide film formation machining, there is a possibility that the Si oxide film comparable to the heat oxide film is obtained.

[0044] (Embodiment 1-4) By using the machining apparatus of the aforesaid Embodiment 1-3, a machining was attempted with Cu, Mo, Fe and Al being made samples. Its machining conditions and machined results are shown in Table 4 below. Under these machining conditions, Cu and Mo were a removal machining, and Fe and Al the oxide film formation machining.

[0045]

[Table 4]

Material to be machined	Machining conditions				Machined results (Specific machined volume: for removal machining) (Oxide film thickness : for oxidation machining)
	DC voltage (kV)	Gap (mm)	Current density (mA/cm ²)	Time (min)	
Cu	1~2	1	400	10	Removal machining (0.29mm ³ /A·min)
Mo	0.5	1	38	60	Removal machining (0.44mm ³ /A·min)
Fe	4.5	1	16	60	Oxidation (Film thickness : 18μm)
Al	6	1	12	60	Oxidation (Film thickness : 15μm)

[0046] Here, surfaces of Cu and Mo machined just after a finish of the machining have changed in their colors respectively to brown and black. It seems that these

are an oxide CuO of Cu and an oxide MoO of Mo . Especially, as to Cu a green mist has appeared in the water during the machining and, further, a blue mist has suspended in a part of the water after the finish of the machining of Mo . Accordingly, it is inferred that surfaces of machined Cu and Mo have been oxidized. From these results, one model of a machining mechanism by the electrode reaction in the ultrapure water is considered. That is, it is a model that, in the ultrapure water, in a substance, first an oxidation occurs owing to the fact that OH^- and H_2O participate, and the machining is changed to the removal machining owing to the fact that its oxide is separated by some reason in which OH^- and H_2O further participate.

[0047] (Embodiment 2) In this embodiment it was attempted to machine the workpiece immersed in the ultrapure water by means of increasing an OH^- concentration in the ultrapure water by maintaining the ultrapure water at a high temperature and under a high pressure. As shown in Fig.1, it is understood that if the water whose density is 1.0 g/cm^3 at 25°C nearing the room temperature and under an atmospheric pressure is raised in its temperature to 200°C while keeping the density constant as it is, the pressure

becomes 3000 atm. Accordingly, as shown in Fig.5, this apparatus is of a structure in which a container 43 made of tetrafluoroethylene resin and filled with an ultrapure water 42 is disposed in an internal reaction chamber 41 of a pressure vessel 40, a sample 44 made of Si is immersed in the ultrapure water 42, a heating ceramic heater 45 is wound around an outer periphery of the pressure vessel 40 and, further, it is covered with a heat insulating material 46, and an electric current is supplied to the ceramic heater 45 through a slidac 47. Incidentally, the temperature is measured by a thermocouple 48 contacted with the pressure vessel 40. The pressure vessel 40 is one which is designed so as to withstand 3000 atm and in which a vessel body 40a having the accommodation space 41 and a lid body 40b are jointed by eight bolts 40c, and the vessel body 40a and the lid body 40b are sealed by a gasket 40d made of Cu. Further, the vessel body 40a and the lid body 40b are made of a stainless steel (SUS 304) and the bolt 40c is made of an HPM 2 steel whose linear expansion coefficient is smaller than the stainless steel, so that it becomes a self-tightening structure in which, when the temperature is raised, a tightening force is increased owing to a difference in thermal expansion coefficient.

[0048] As the above sample 44, a Si wafer of 400 μm in thickness and 1 x 2 cm in longitudinal and transverse lengths is used. As a pretreatment, first an oil component and another contamination on the surface of the Si wafer were wiped off by ethyl alcohol, and next an oxide film was removed by cleaning with 5% hydrofluoric acid for 30 seconds. And, finally it was cleaned in the ultrapure water (flowing water) for 10 seconds and sufficiently dried. Before machining, a weight of this Si wafer was measured in mg order. Machining conditions and machined results as a weight before machining and a weight after machining are shown in Table 5 below.

[0049]

[Table 5]

Machining conditions				Machined results		
Water temperature	Pressure	Ion product	Time	Weight before machining	Weight after machining	Thickness reduction amount
200°C	3000 atm	10.118	1 hr	329 mg	327 mg	2.1 μm

[0050] Here, in regard to the machining time, after a thermocouple monitor had indicated 200°C, it was waited (for 10 minutes) until the temperature of the ultrapure water in the internal reaction chamber became 200°C and, thereafter, a machining was performed for 1 hour. Further, the thickness reduction amount in the table was calculated by mass

difference/(density x surface area).

[0051] (Embodiment 3) A machining of a Cu plate was attempted by using such a machining apparatus as shown in Figs.6(a) and (b). This machining apparatus has a structure in which a platinum electrode plate 52 becoming cathode and a Cu made sample 53 becoming anode are immersed in an ultrapure water 51 filled in a container 50 with a constant gap being held between them, a cation exchange membrane (Nafion 117) 54 is arranged between both electrodes, the whole of the container 50 is accommodated in a gas tight container 55, and its inside is purged by Ar gas. More detailedly, the platinum electrode plate 52 is fixed with the cation exchange membrane 54 being put between it and one side face side of a gap spacer 56 whose inside is opened, the sample 53 is fixed to the other side face side of the gap spacer 56, and under this state they are immersed in the ultrapure water 51. In this case, the ultrapure water 51 is filled also in an opening 56a of the gap spacer 56. And, a DC voltage was applied between the platinum electrode plate 52 and the sample 53 from an electric source 57 such that an electric current value becomes constant during the machining. Machining conditions and machined results are shown in Table 6 below.

[0052]

[Table 6]

	Machining conditions			Machined results
	Opposing area	Gap	Current value	Specific machined volume
Machining 1	1×4.5 (cm ²)	2 mm	40 mA	2.35 mm ³ /A·min
Machining 2	1×9 (cm ²)	2 mm	30 mA	0.83 mm ³ /A·min

[0053] Here, in the Machining 1 in Table 6, as a result that the machining was performed by immersing the cation exchange membrane in the ultrapure water with it being dried intact, when the cation exchange membrane was observed after finishing the machining, the cation exchange membrane expanded toward a sample side only in its portion contacting with the ultrapure water by absorbing the water. As a result, there was almost no gap between the cation exchange membrane and the sample. In contrast to this, in the Machining 2 in Table 6, the cation exchange membrane was set to the gap spacer after it had been preliminarily immersed in the ultrapure water for a sufficient time to thereby uniformize an expansion of the membrane and, thereafter, further cleaned sufficiently by the ultrapure water. As a result, in the Machining 1 the voltage applied in order to ensure a current value of 40 mA was several 10s V, whereas in the Machining 2 the voltage applied in order to ensure a current value

of 30 mA became 600 to 1400 V.

[0054] In the machining method in which the OH^- ion concentration is increased by this ion exchange treatment, if a specified shape tool having on its surface an ion exchange material is made the cathode and the workpiece is made the anode, a machining capable of transcribing the shape of the tool to the workpiece (transcription machining) is possible and, if a wire electrode having on its surface the ion exchange material is used as the cathode, a machining capable of cutting the workpiece of the anode (cut machining) is possible.

[0055]

[Effects of the Invention] According to the machining method by hydroxyl group in ultrapure water of the invention, which is constituted in such a manner as mentioned above, there are brought about remarkable effects mentioned below.

(1) Since it is the machining by the chemical action between the OH^- ions and the workpiece, properties of the workpiece are not deteriorated.

(2) Differing from an aqueous solution used in the electrolytic machining and the like, since in the ultrapure water there exist only H^+ , OH^- and H_2O and no impurities such as metal ions exist, if an

interception of the impurities from outside is complete, the machining in a completely clean atmosphere is possible.

(3) Since only the ultrapure water is used, a great reduction in machining cost is possible as well.

[Brief Description of the Drawings]

[Fig.1] It is a graph showing a relation between density and ion product of a water with temperatures and pressures being made parameters.

[Fig.2] It is a simplified sectional view of a machining apparatus in which an electrolytic machining is adopted as a hydroxyl group increase treatment and a rotary electrode is used.

[Fig.3] It is a simplified sectional view of a machining apparatus in which the electrolytic machining is adopted as the hydroxyl group increase treatment and parallel flat plate electrodes are used.

[Fig.4] It is a simplified sectional view of a machining apparatus in which the electrolytic machining is adopted as the hydroxyl group increase treatment and a needle-like electrode is used.

[Fig.5] It is a simplified sectional view of a machining apparatus in which a high temperature and high pressure treatment is adopted as the hydroxyl group increase treatment.

[Fig.6] It shows a machining apparatus in which an ion exchange treatment is adopted as the hydroxyl group increase treatment, wherein (a) is a simplified sectional view of the apparatus, and (b) an exploded perspective view showing a structure around an electrode.

[Description of the Reference Numerals and Signs]

1 sample (workpiece)	2 rotary electrode
3 water tank	4 ultrapure water
5 XY stage	6 support member
7 Z stage	8 motor
9 rotation shaft	10 electric source
11 lead wire	12 ammeter
13 gas tight chamber	
20 container	21 ultrapure water
22 sample (workpiece)	23 spacer
24 electric source	25 lid
26 bag	27 thermometer
30 sealed container	31 water tank
32 ultrapure water	33 holding base
34 sample (workpiece)	35 needle-like electrode
36 electric source	37 thermometer
40 pressure vessel	
40a vessel body	40b lid body
40c bolt	40d gasket

41 internal reaction chamber 42 ultrapure water
43 container 44 sample (workpiece)
45 ceramic heater
46 heat insulation material
47 slidac 48 thermocouple
50 container 51 ultrapure water
52 platinum electrode plate 53 sample (workpiece)
54 cation exchange membrane 55 gas tight container
56 gap spacer
56a opening
57 electric source

[Fig.1]

(a) ION PRODUCT

(b) DENSITY

[Fig.2]

10 ELECTRIC SOURCE

[Fig.3]

24 ELECTRIC SOURCE

[Fig.4]

36 ELECTRIC SOURCE

[Fig.5]

47 SLIDAC

(a) TEMPERATURE MONITOR

[Fig.6]

57 ELECTRIC SOURCE

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